

Supporting Information

Long-Range Electron Tunneling

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Semiclassical ET theory predicts that reactants will have identical configurations at the transition state for an electron-exchange reaction. For the electron exchange reaction between Fc and Fc^+ in the gas phase, this configuration is defined as Q^\ddagger (Figure S1). The energy required to reach this

$$\lambda_1 = \frac{1}{2}k(Q - Q_0)^2$$

configuration is equal to $\lambda_1 + \lambda_2$, where and

where k is an arbitrary force constant. The

$$\lambda_2 = \frac{1}{2}k[Q - (Q + \delta_Q)]^2,$$

transition state configuration (Q^\ddagger) corresponds to a

$$Q^\ddagger = Q_0 + \frac{1}{2}\delta_Q$$

minimum value of $\lambda_1 + \lambda_2$, found by differentiation:

The ionization energy at Q^\ddagger is given by:

$$IE(Q^\ddagger) = E_{00} + \frac{1}{2}k[Q^\ddagger - (Q_0 + \delta_Q)]^2 - \frac{1}{2}k(Q^\ddagger - Q_0)^2.$$

Simplification gives the following result:

$$IE(Q^\ddagger) = E_{00}$$

Hence, the Fc ionization energy at the electron-exchange transition state is best approximated by the adiabatic ionization energy.

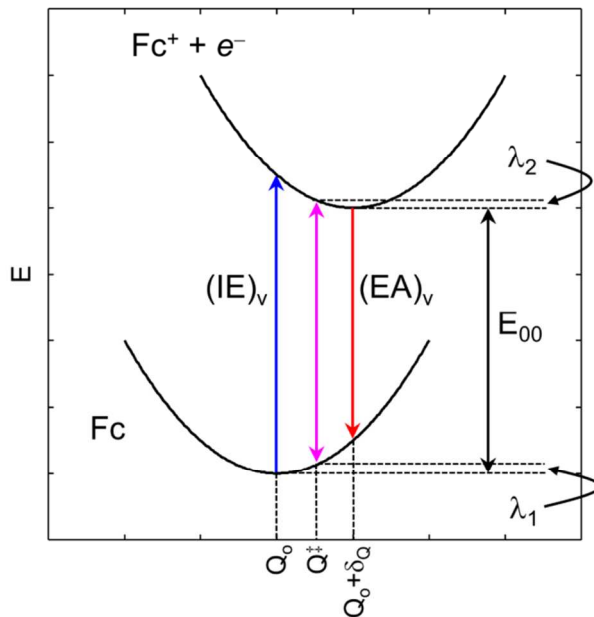


Figure S1. Gas-phase potential energy surfaces for Fc and $\text{Fc}^+ + e^-$ illustrating the vertical ionization energy $(IE)_v$ and electron affinity $(EA)_v$. The electron-transfer transition state configuration is Q^\ddagger .

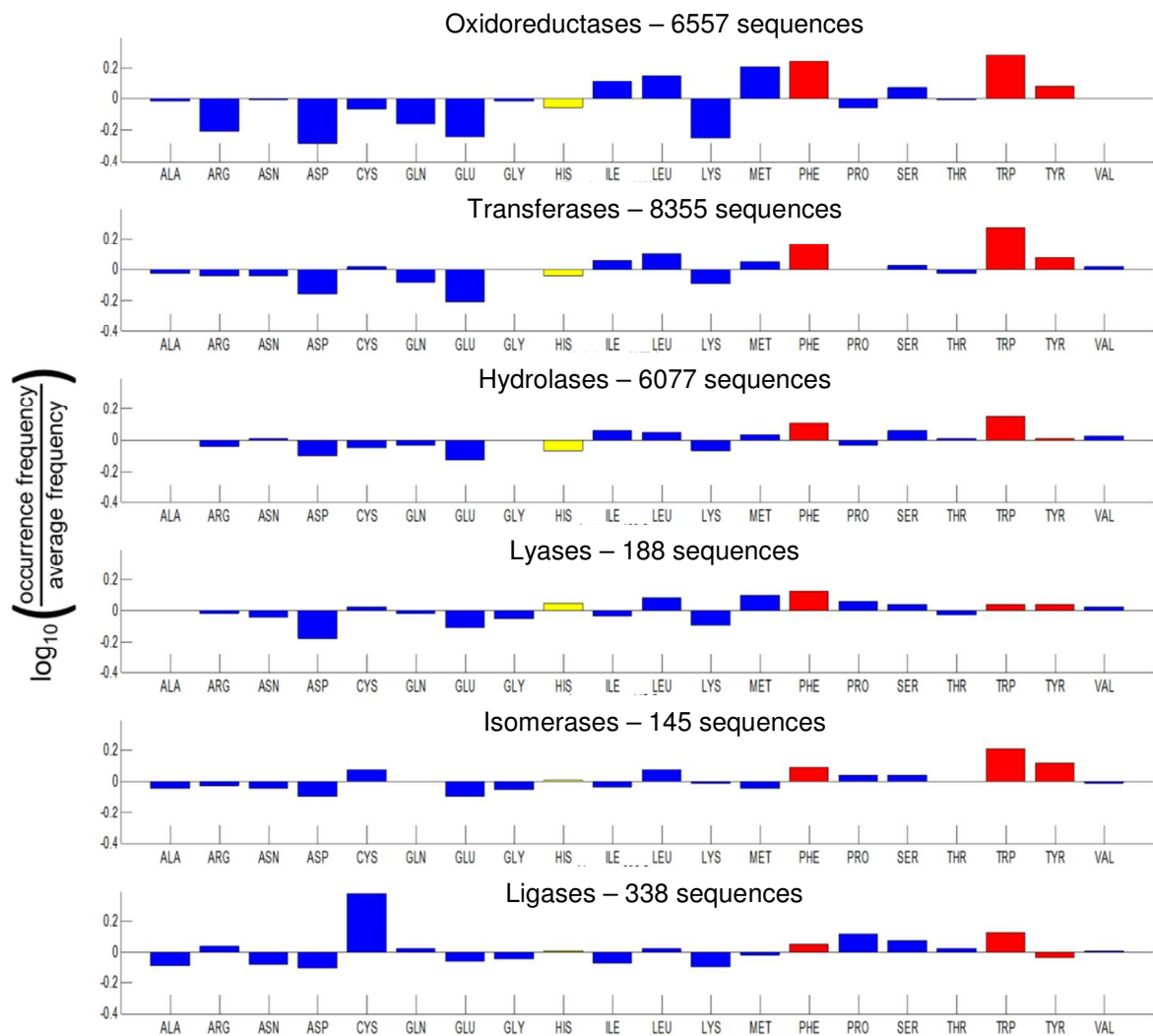


Figure S2. Amino-acid occurrence frequencies in enzymes with transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

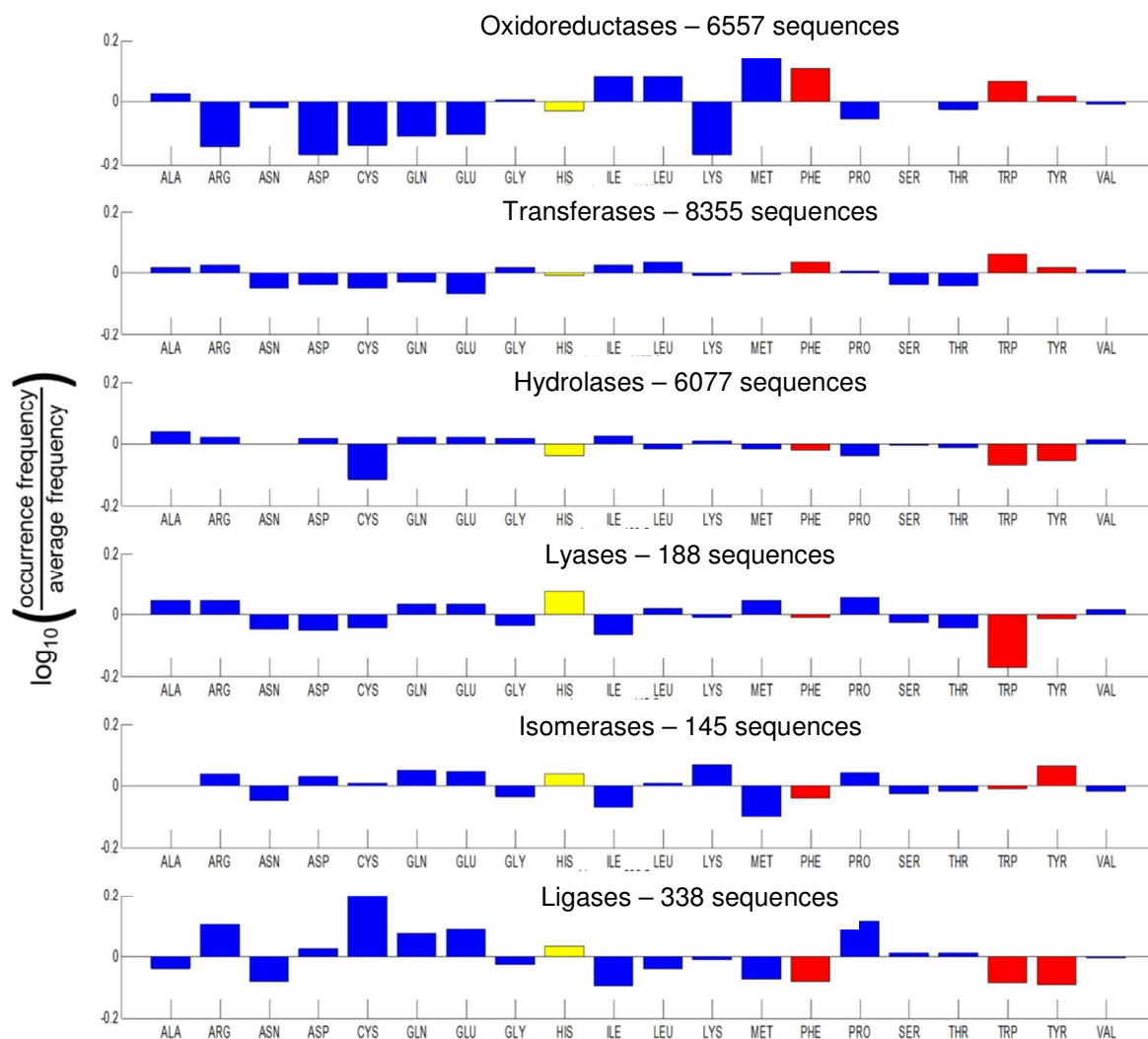


Figure S3. Amino-acid occurrence frequencies in enzymes with transmembrane segments relative to the average frequencies of enzymes with transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

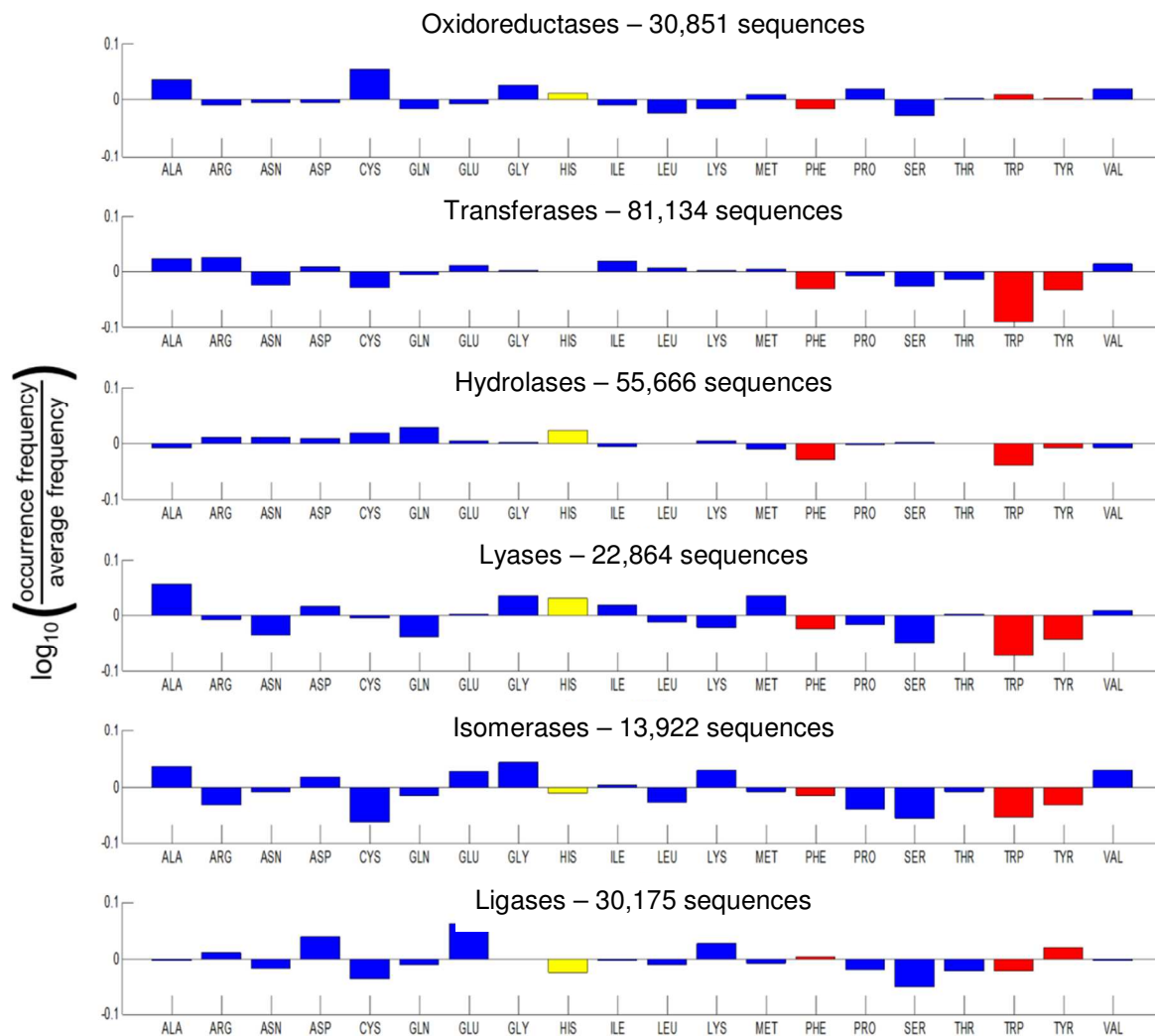


Figure S4. Amino-acid occurrence frequencies in enzymes without transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

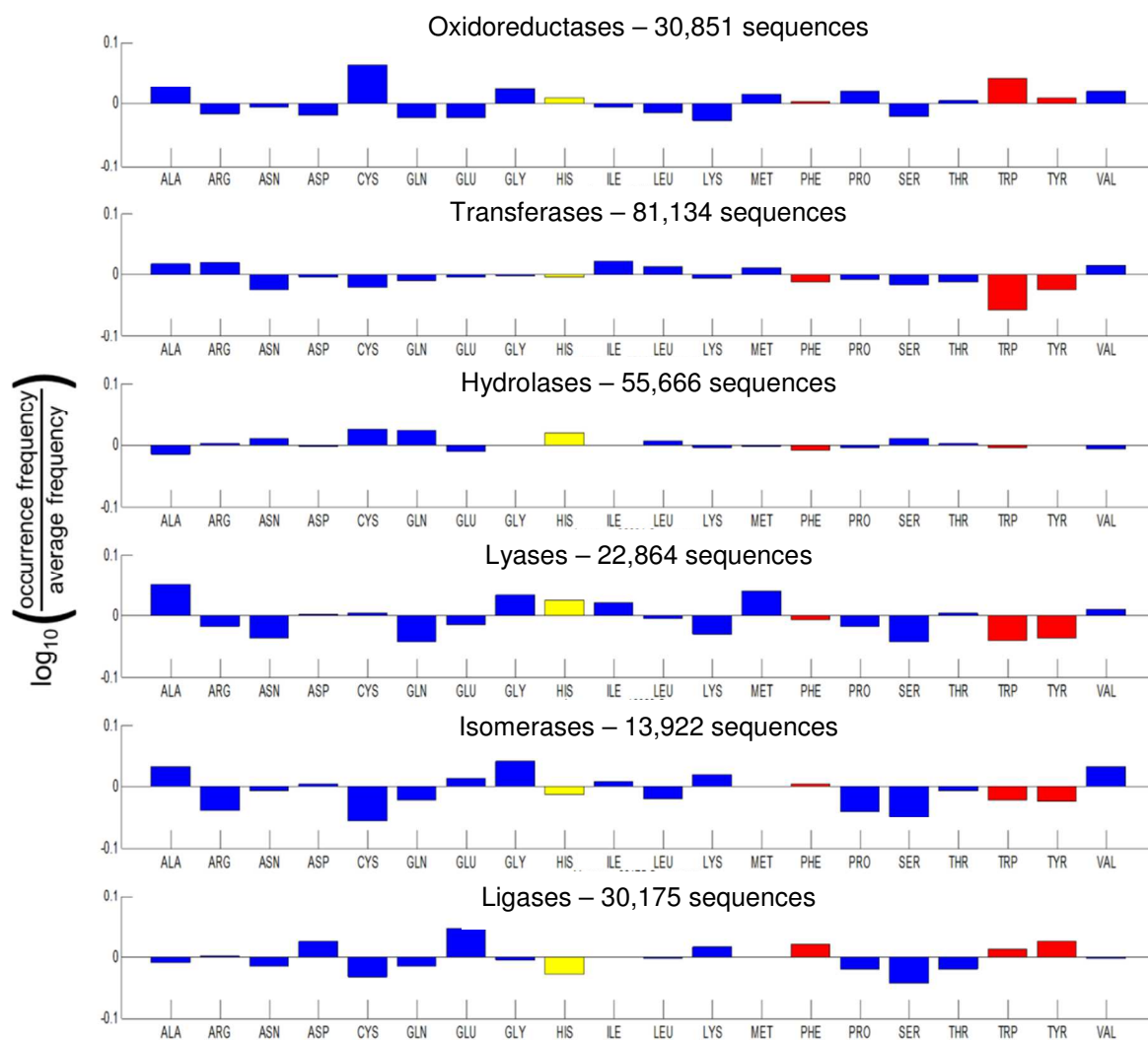


Figure S5. Amino-acid occurrence frequencies in enzymes without transmembrane segments relative to the average frequencies of enzymes without transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

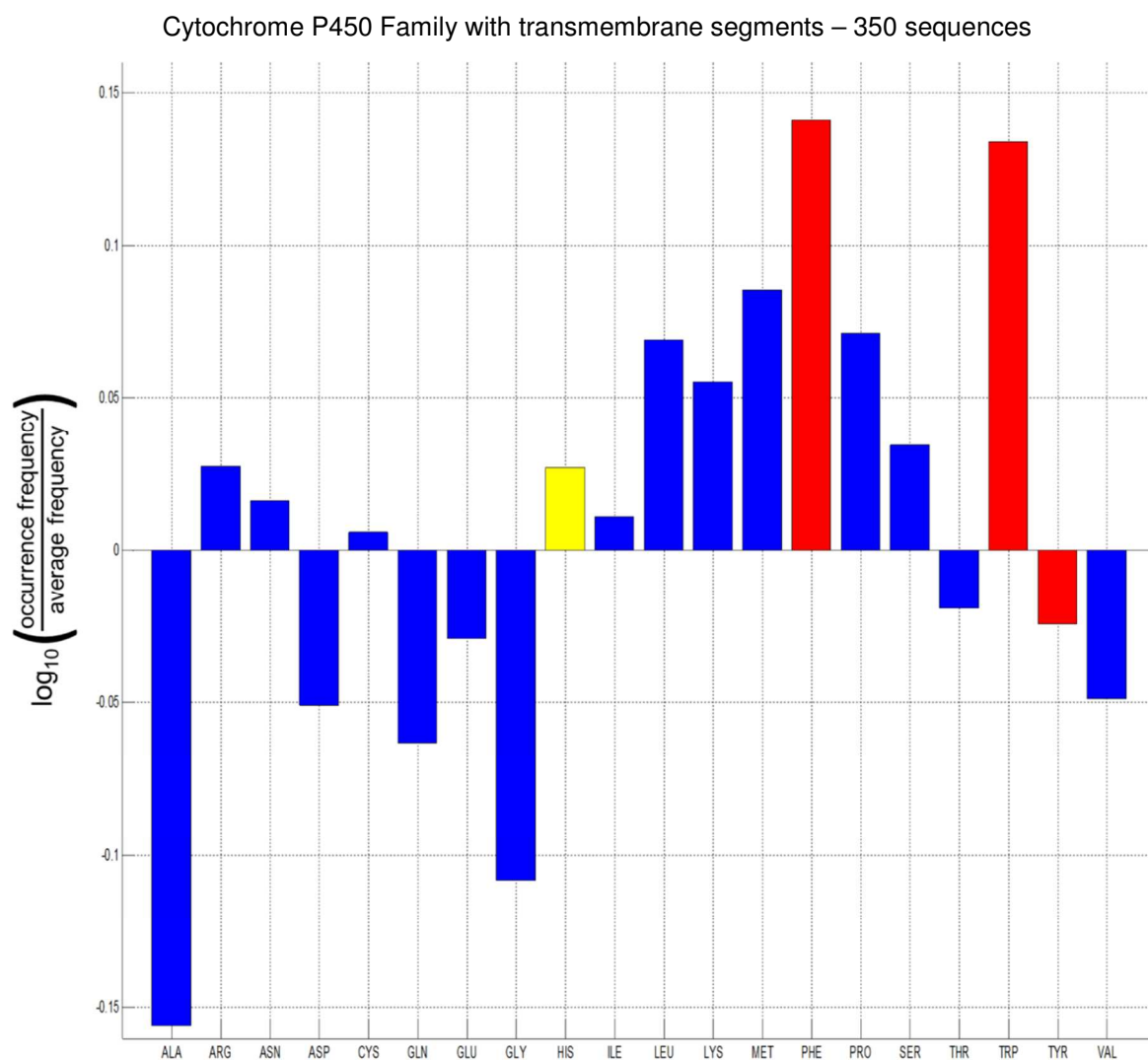


Figure S6. Amino-acid occurrence frequencies in the primary sequences of the cytochrome P450 family of enzymes with transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

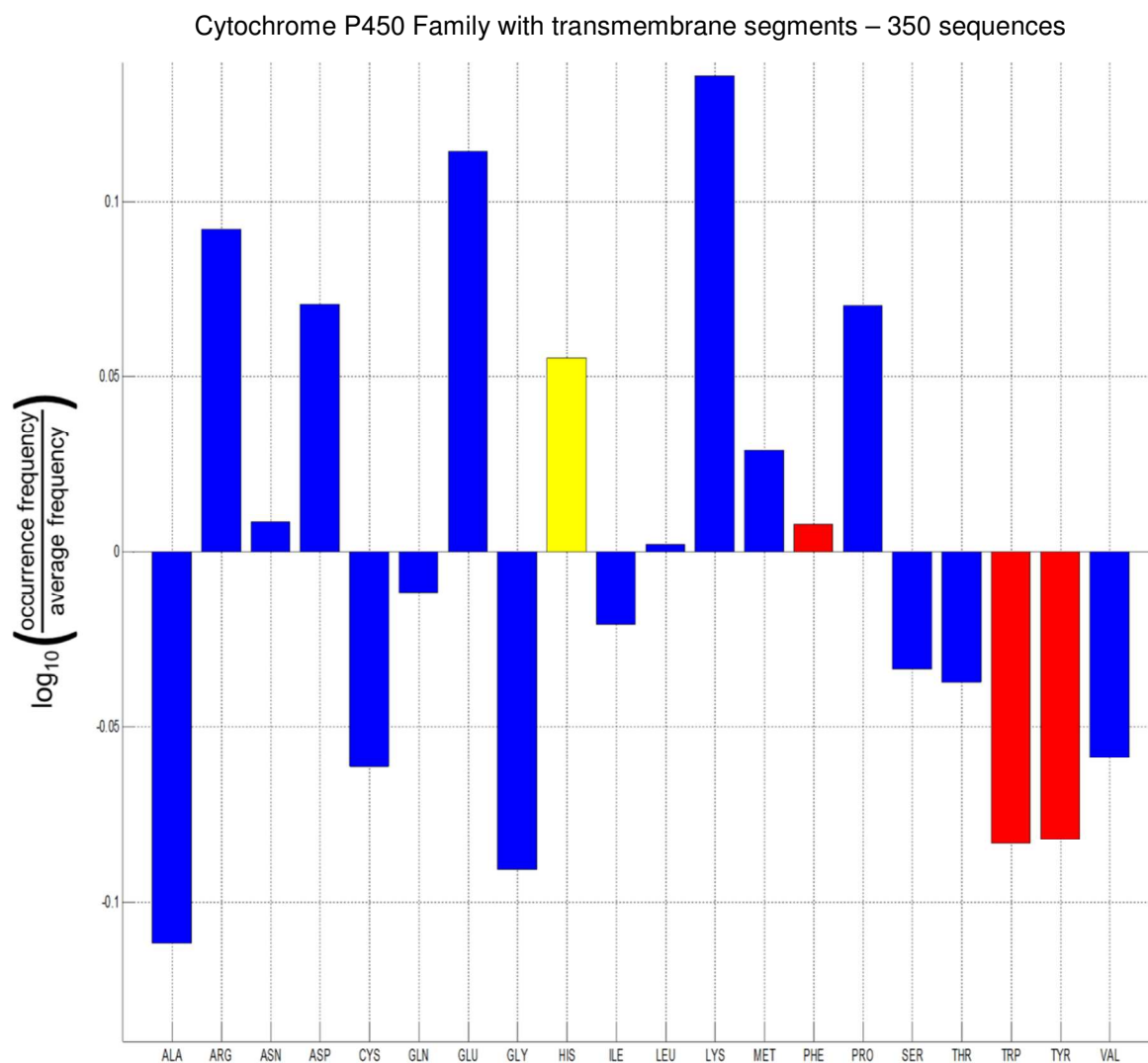


Figure S7. Amino-acid occurrence frequencies in the primary sequences of the cytochrome P450 family of enzymes with transmembrane segments relative to the average frequencies of enzymes with transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

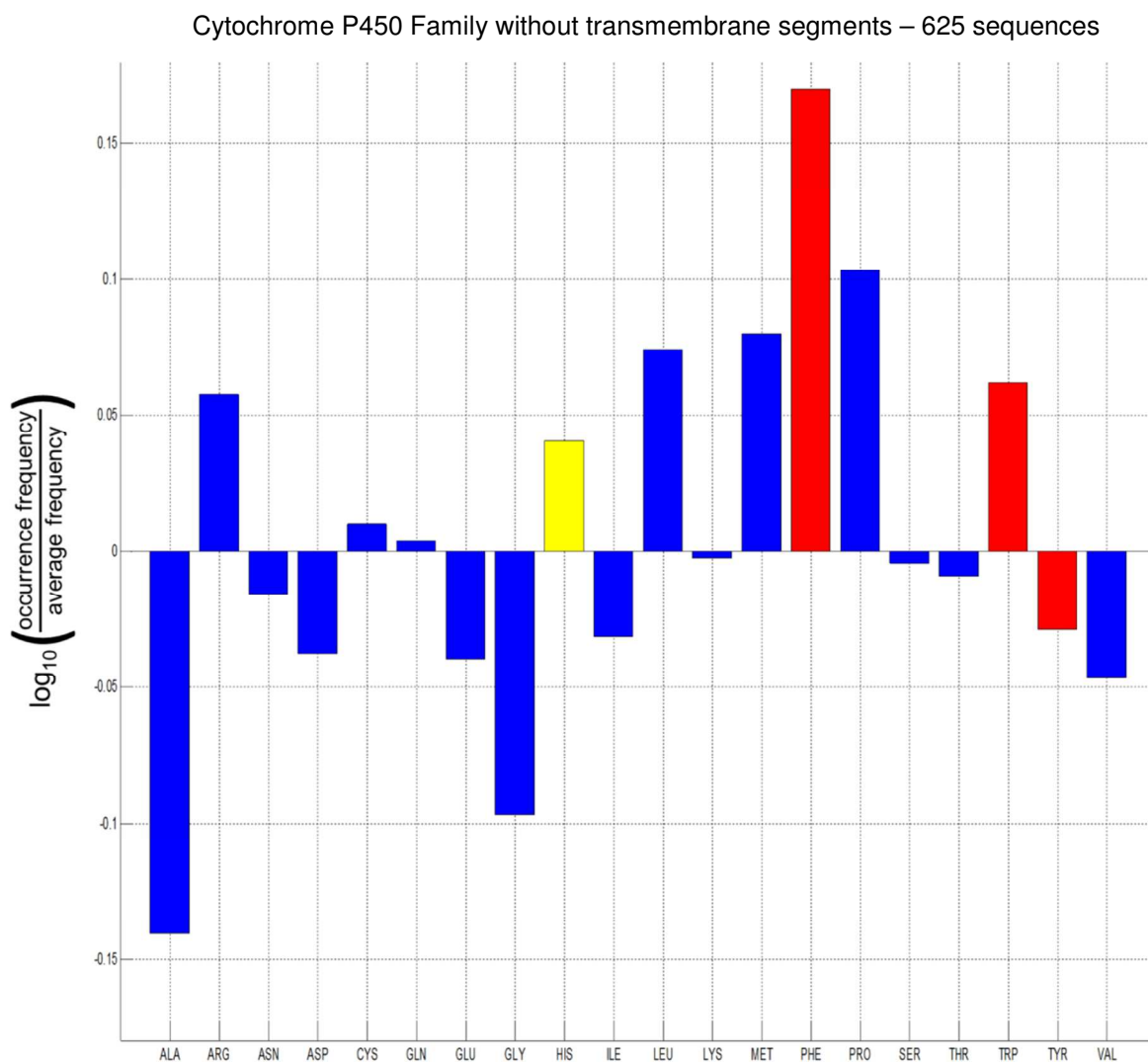


Figure S8. Amino-acid occurrence frequencies in the primary sequences of the cytochrome P450 family of enzymes without transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

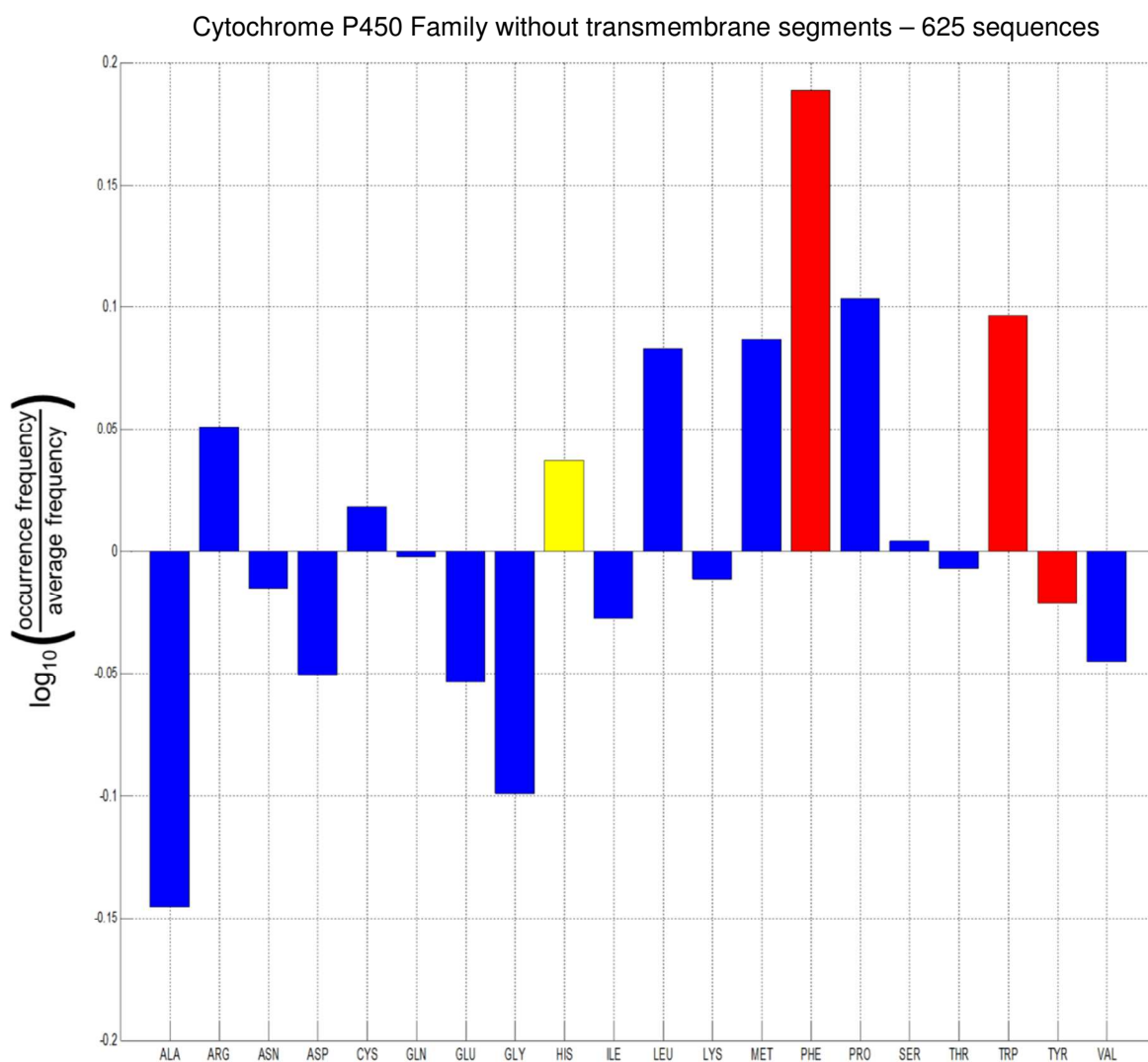


Figure S9. Amino-acid occurrence frequencies in the primary sequences of the cytochrome P450 family of enzymes without transmembrane segments relative to the average frequencies of enzymes without transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

O₂⁻ and H₂O₂-reactive enzymes with transmembrane segments – 1648 sequences

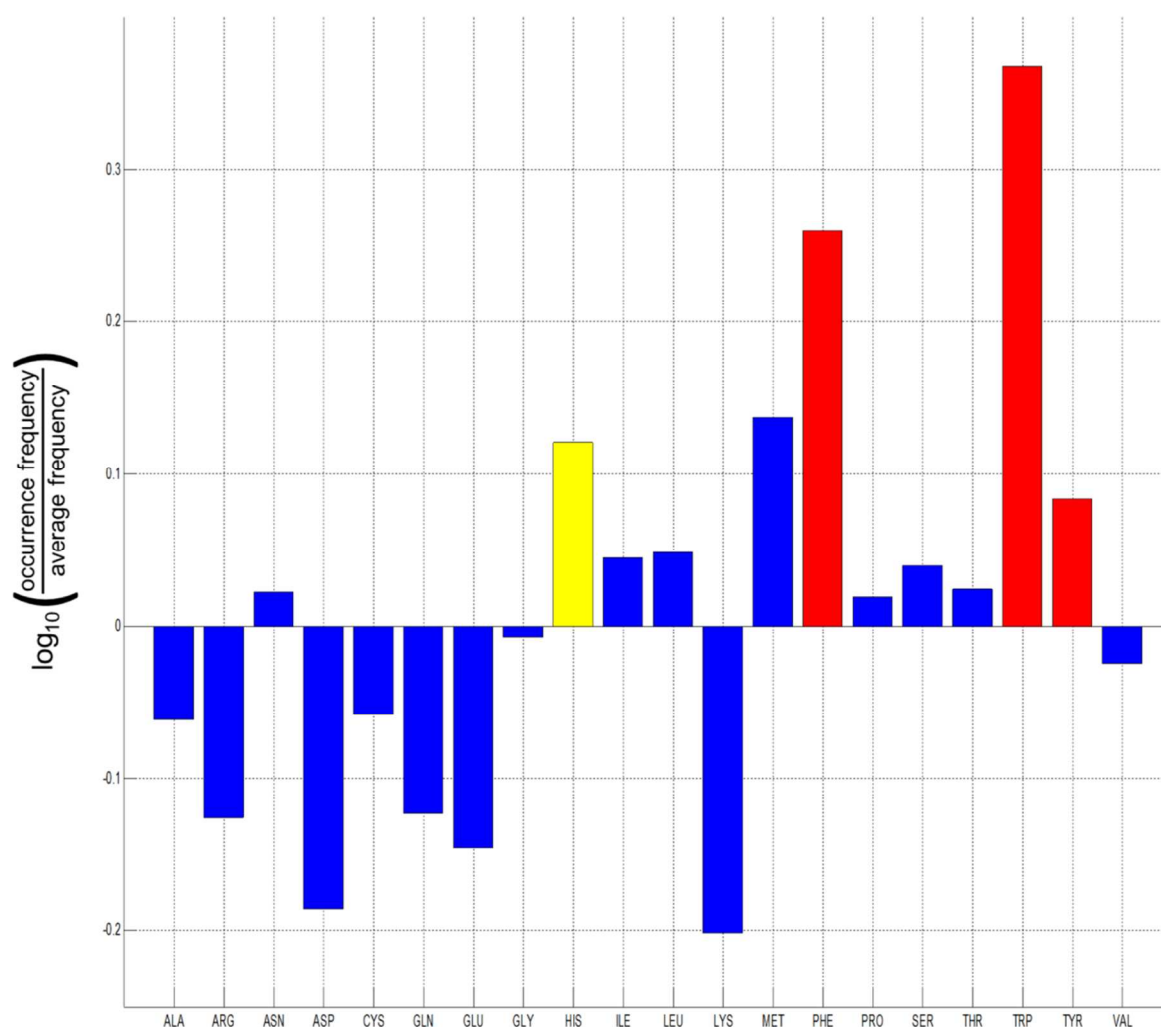


Figure S10. Amino-acid occurrence frequencies in the primary sequences of O₂⁻ and H₂O₂-reactive enzymes with transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

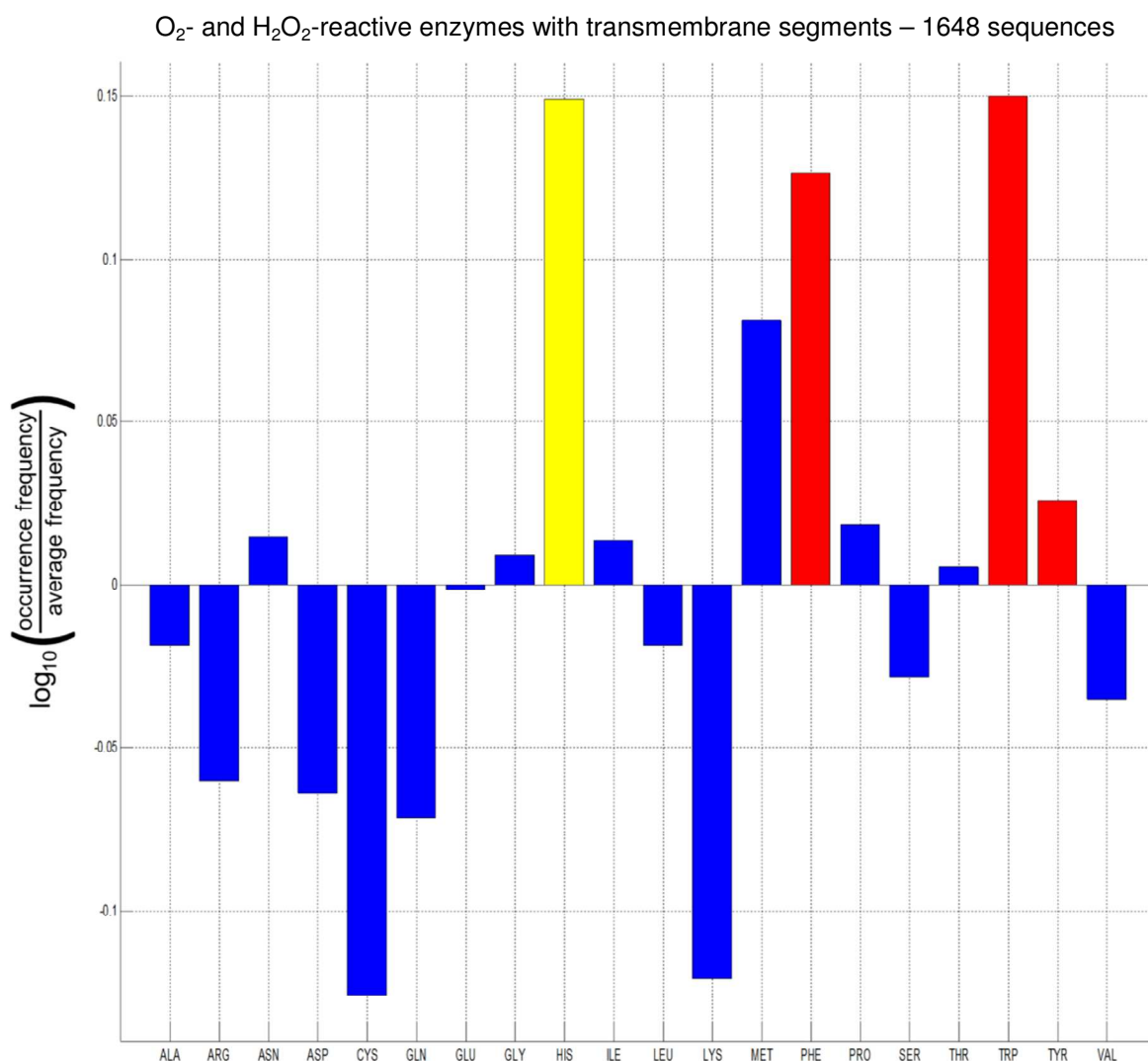


Figure S11. Amino-acid occurrence frequencies in the primary sequences of O₂- and H₂O₂-reactive enzymes with transmembrane segments relative to the average frequencies of enzymes with transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

O₂⁻ and H₂O₂-reactive enzymes without transmembrane segments – 5501 sequences

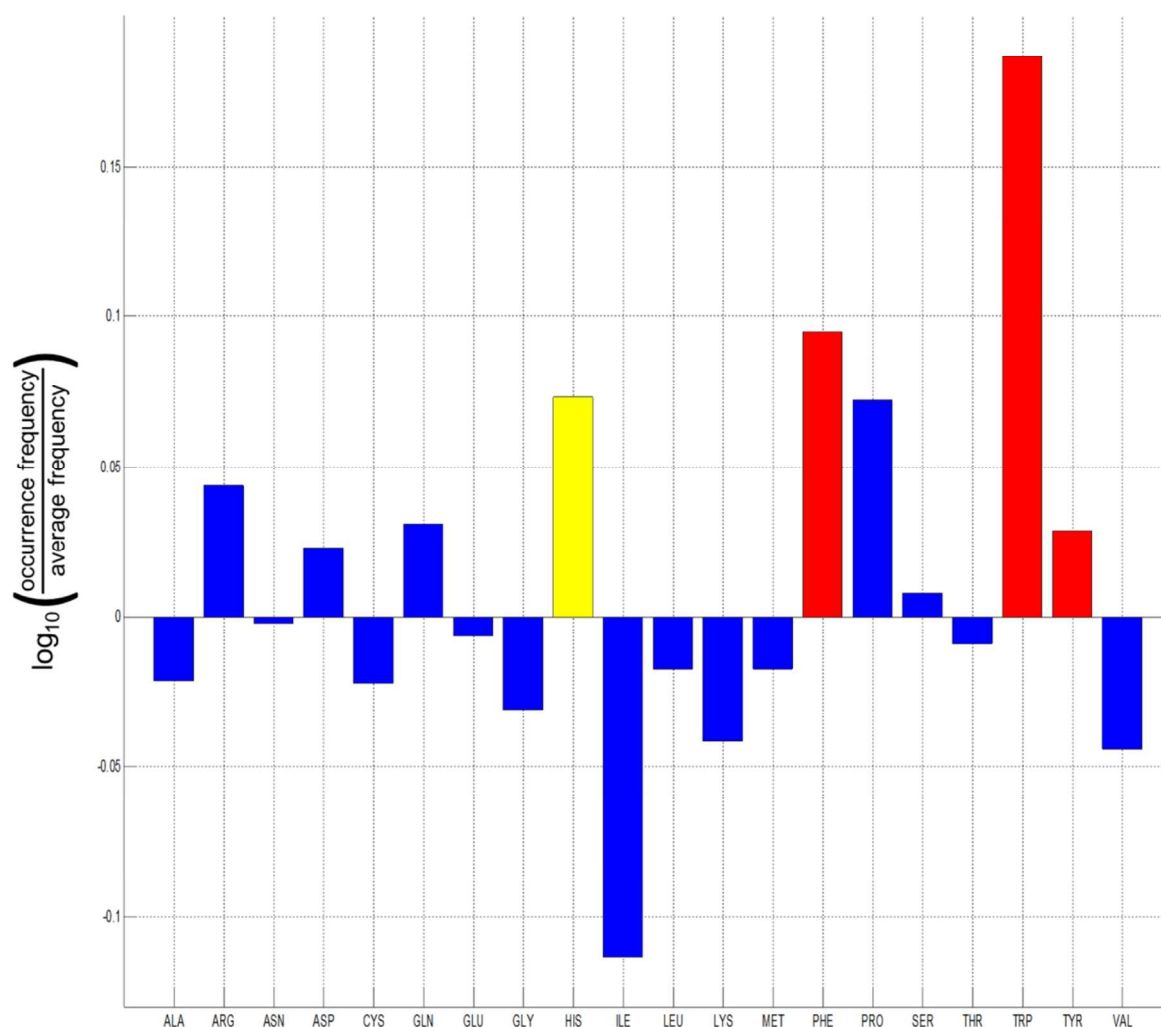


Figure S12. Amino-acid occurrence frequencies in the primary sequences of O₂⁻ and H₂O₂-reactive enzymes without transmembrane segments relative to the average frequencies in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).

O₂⁻ and H₂O₂-reactive enzymes without transmembrane segments – 5501 sequences

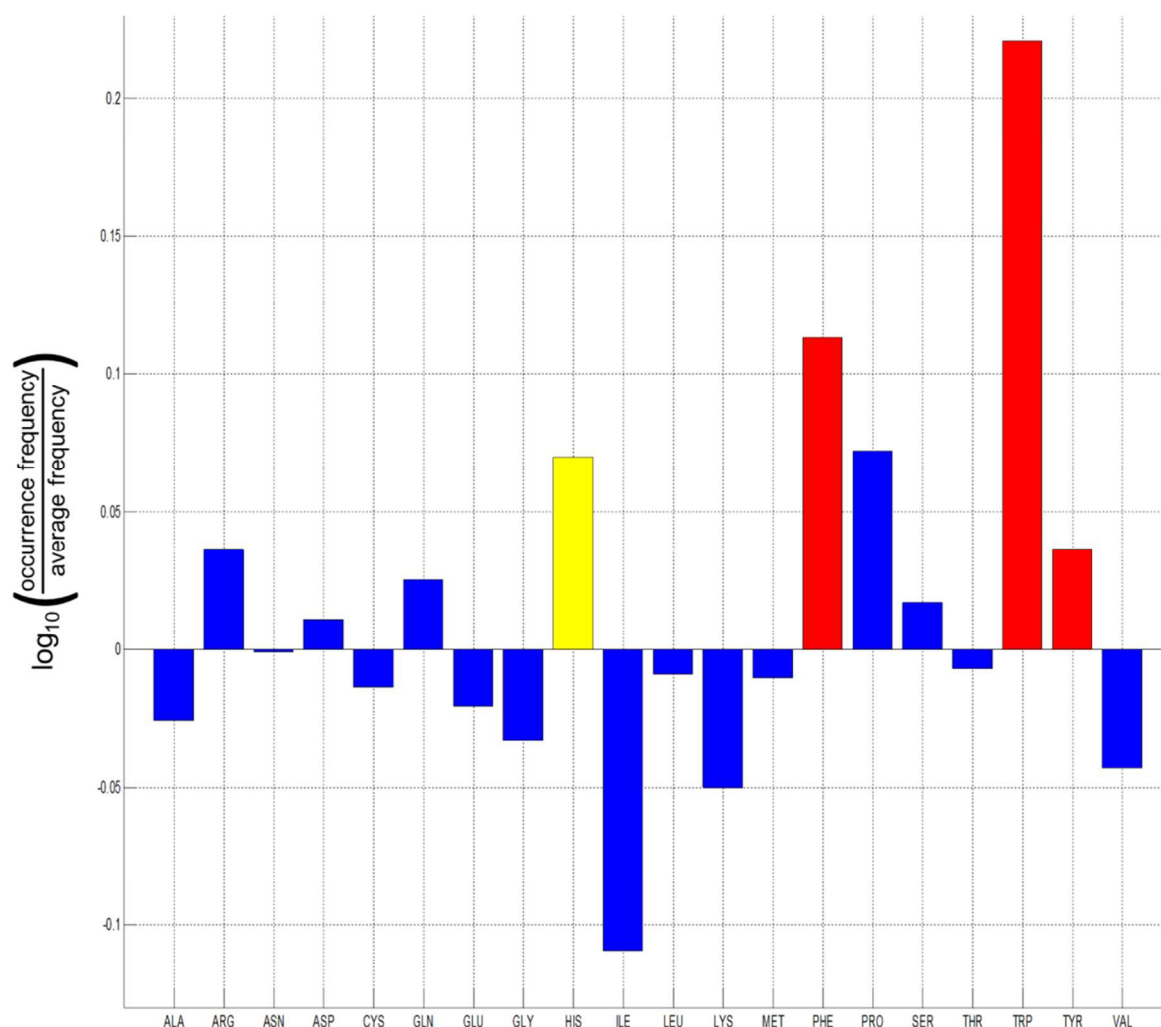


Figure S13. Amino-acid occurrence frequencies in the primary sequences of O₂⁻ and H₂O₂-reactive enzymes without transmembrane segments relative to the average frequencies of enzymes without transmembrane segments in the Enzyme Data Bank of the Swiss Institute of Bioinformatics (<http://www.uniprot.org/>).